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Growth defects in pure and mixed crystals of KDP-ADP by X-ray Lang Topography

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Abstract : A full series of compositions of KDP-ADP mixed crystals were grown by slow evaporation method. Crystals having habitual faces were grown from the end composition. X-ray topographs of pure KDP, pure ADP and mixed KDP-ADP were taken by Lang transmission method. Apart from dislocations, growth imperfections such as growth bands, lattice deformation at the boundary between two growth sectors (prismatic and pyramidal) and inclusions present in the crystal were observed and analysed.

Keywords : Solution growth, mixed KDP-ADP, X-ray Lang Topography

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1. Introduction

The study of mixed crystals of Potassium Dihydrogen Orthophosphate and Ammonium Dihydrogen Orthophosphate (KDP : ADP) has attracted considerable attention during recent years due to their wide spread applications in quantum electronics and optoelectronics. A lot of studies have been reported by several workers on KDP and ADP crystals [1,2]. We have also done some work on pure KDP and ADP in the light of their physical property like microhardness [3] and dielectric constant measurements [4]. Apart from this some defect characterization studies by chemical etch pit method have also been reported by us [5,6]. But only very few reports are available during the last several years on mixed KDP : ADP system [4,7-12]. Recently the study of variation of microhardness number with load for a wide range of composition for solution grown mixed KDP-ADP crystal has been done by us [13]. Beside this, the variations of lattice parameters with composition using X-ray diffraction technique were studied by some workers [4,14,15]. Chemical etching technique has also been applied with greater details to reveal dislocations in mixed system [16,17].

To asses the quality of the crystals in terms of grown-in-defects on planar habit faces of pure KDP and pure ADP crystals, extensive X-ray topographic studies (XRT) [18,19] have been made in past years [20–25]. Very little work has been done on XRT of mixed KDP-ADP system with variations of compositions [26].

In the present work, we have done topography work on as-grown single crystals of pure and mixed KDP-ADP system by Lang transmission method [27–29]. Similar to KDP type crystals [25], we have also observed clear growth sector boundaries and growth bands along with dislocations originating from inclusions and the crystal seed.

2. Crystal growth

Saturated solutions of various compositions ranging from 5% ADP to 95% ADP were mixed with KDP solutions and allowed for slow evaporation. Crystals having habitual faces have been harvested from the end compositions. Needles type crystals were obtained at the intermediate range.

Thin '*c*' cut plates of the samples with dimensions about 8 mm × 7 mm × 2 mm were prepared from good quality crystals grown by slow evaporation. For each composition three different projection topographs were taken with 222, 020 and 022 reflections on Ilford G5 nuclear emulsion plates, using a Rigaku X-ray topographic camera and Radon House X-ray generator with MoKα (λ = 0.7107 Å). Recorded plates were developed with Kodak D19b developer, and enlarged in Carl-Zeiss optical microscope.

3. Results and discussion

Figures 1 (a, b, c) show X-ray topographs of (001) plate of a KDP crystal cut very near to the seed region with a string saw. The cut surfaces were polished by gently moving the plate on a soft moist cloth wetted with a mixture of 50% ethyl alcohol and 50% double distilled water. In Figure 1 (a, b) the position of the seed can be detected through a strong constrast. All the growth sectors and boundaries between the prismatic and the pyramidal regions are very clear with good contrast. The starting points of dislocations propagating in the four growth sectors are also seen. These topographs have been compared with a schematized representation of all kinds of growth bands and sector boundaries as shown in Figure 2 [25].

It is found that in Figures 1a and 1b (200 and 020 reflection), numerous growth bands with different contrasts are clearly visible in the two opposite pyramidal sectors. Well-resolved dislocation lines originating from seed have also been observed on pyramidal faces in (200) and (020) reflections. Growth sector boundaries are revealed by black or white contrast in the case of symmetric reflections (200 and 020), while with asymmetric reflection (022) boundaries become faint and contrast is not visible (Figure 1c), due to oblique angular projections.

Plate I

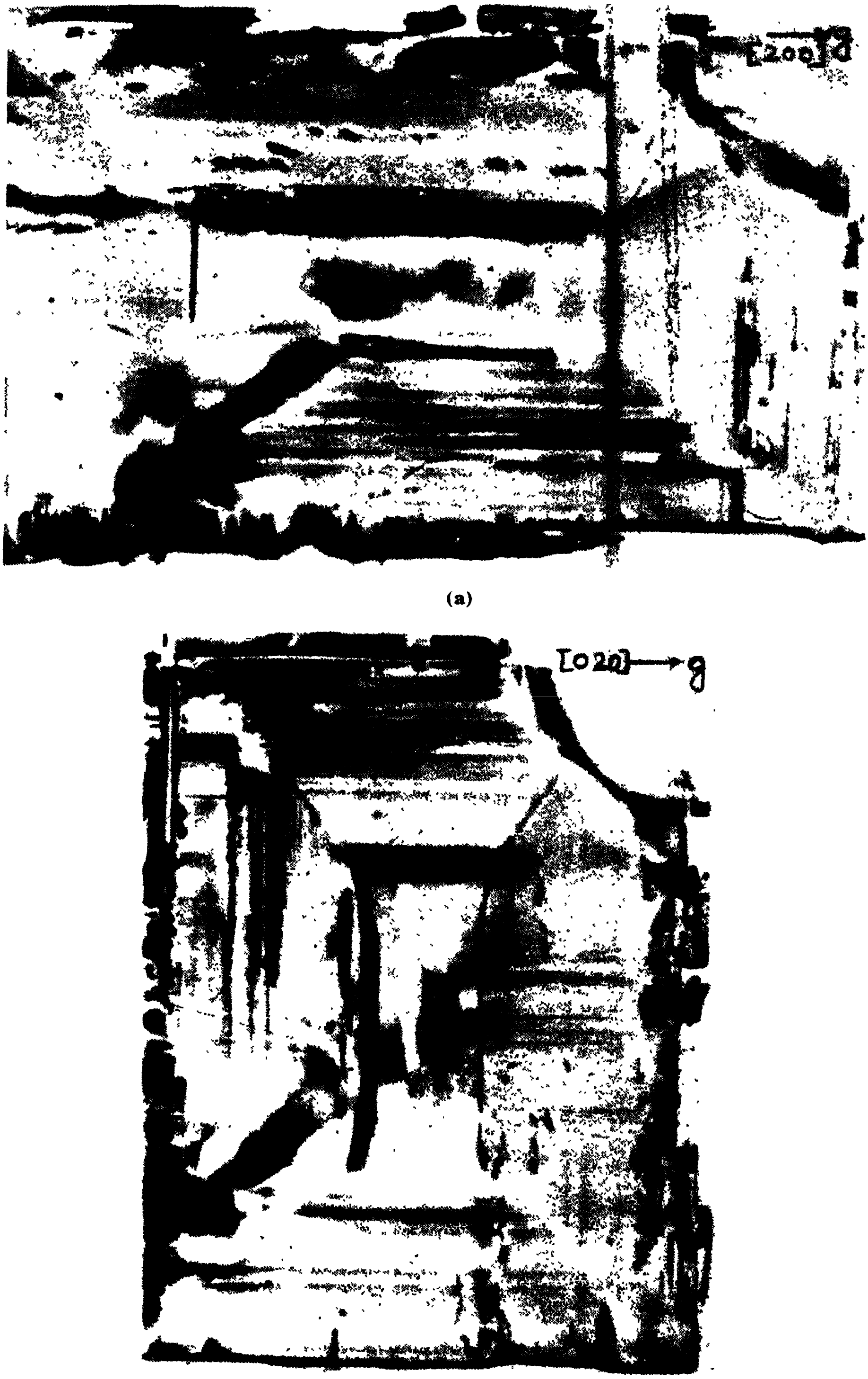

Figure 1. X-ray topographs of (001) section of pure KDP crystal for (a) (200) and (b) (020) reflection.

Plate I (Cont'd.)

(c)

Figure 1. X-ray topographs of (001) section of pure KDP crystal for (c) (022) reflection.

Usually in solution-grown KDP and ADP crystals, these kinds of growth bands and sector boundaries have been observed in both prismatic and pyramidal sectors [21,23,25]

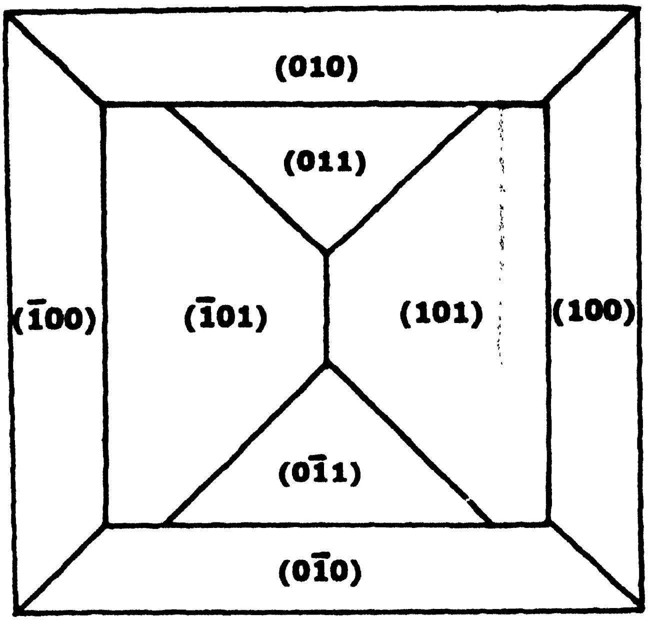

Figure 2. Schematic representation of the growth sectors and the boundaries between them for an idealized situation of projection on the (001) plane in X-ray transmission topographs

and correlated bands with the impurity content in these growth sectors [21,22]. Due to the variations of supersaturation, prismatic growth sector consists of successive layers largely different in their impurity content and consequently well-depicted contrasting bands are visible in the topographs. Both growth bands and sector boundaries originate from lattice deformations due to a difference in lattice parameters in adjacent regions caused by a local variation in impurity content, which leads to local strain field in these crystal areas. It has been concluded from X-ray diffraction topography, that the strain field around these sector boundaries can arise in two ways : (i) by a slight angular misorientation between two neighbouring sectors or (ii) by a distortion in lattice parameter due to a segregation of impurities leading to a difference in unit cell parameters between adjacent sectors [21].

Figure 3(a) shows the topographs of (001) slice of pure ADP crystal cut far from the seed. All the topographs show the perfection of crystal as few liquid inclusions are visible. Local variation of supersaturation and sudden fluctuation in growth conditions also lead to liquid inclusions in the case of crystals grown from solution. It was observed that a strain has developed around the central nucleation point and also around few inclusions which are trapped in the crystal during growth. Bunches of dislocations also emerge from the seed and inclusions [27]. By comparing the Figure 3(a) with the Figure 3(b), (taken from the plane (022)), it is clearly observed that the dislocations emerging from the inclusion disappears in topograph (Figure 3b). The invisibility proves the fulfilment of the criteria of $\boldsymbol{g}.\boldsymbol{b} = 0$ (minimum contrast). In Figure 3a, Burger vector ($\boldsymbol{b}$) is neither parallel nor perpendicular to the dislocation line direction l, revealing that dislocations are of mixed type. Figure 4 (a, b) show the topographs of ADP-KDP mixed crystals (KDP-95%, ADP-5%) for (200) and (020) reflection. In these topographs the position of the seed is found to be eccentric which may be due to the difference in growth rates between two opposite growth sectors. This difference will also lead to misorientation between growth sectors. These growth bands in all the topographs are aligned normal to the growth directions. In this case the impurities present in the individual components (ADP content) will play an important role in the creation of growth bands in the pyramidal growth sectors. The visibility of growth bands in the topographs of (200) and (020) reflections show that the lattice displacement due to these growth bands are parallel to [100] and [010] respectively.

4. Conclusions

We have characterised the general features of grown-in defects in crystals grown on planar habit faces with the help of Lang X-ray topography techniques. The common defects such as dislocations, growth bands, growth sector boundaries, liquid inclusions *etc* have been clearly observed on KDP, ADP and also on mixed KDP-ADP crystals. The types of dislocations on ADP crystals were found to be of mixed type although detailed analysis from $g.b$ criterion from a number of topographs is necessary to arrive at the characterizations of the dislocations revealed in as-grown crystals. It is very clear that the growth imperfections like growth bands, growth sector boundaries as revealed by XRT present in the ADP-KDP mixed crystals are very similar to those in the pure systems.

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References

[1] R D Deslattes, J L Torgeson, B Paretzkin and A T Horton *J. Appl. Phys.* **37** 541 (1966)

[2] K V Ramaiah and K B R Varma *Bull. Mater. Sci.* **5** 147 (1983)

[3] S Sen Gupta and S P Sen Gupta *Bull. Mater. Sci.* **15** 333 (1992)

[4] S Sen Gupta, T Kar and S P Sen Gupta *Mater. Chem. Phys.* (accepted) (1999)

[5] S Sen Gupta, T Kar and S P Sen Gupta *J. Mater. Sci.* **27** 5935 (1992)

[6] S Sen Gupta, T Kar and S P Sen Gupta *Jpn. J. Appl. Phys.* **32** 1160 (1993)

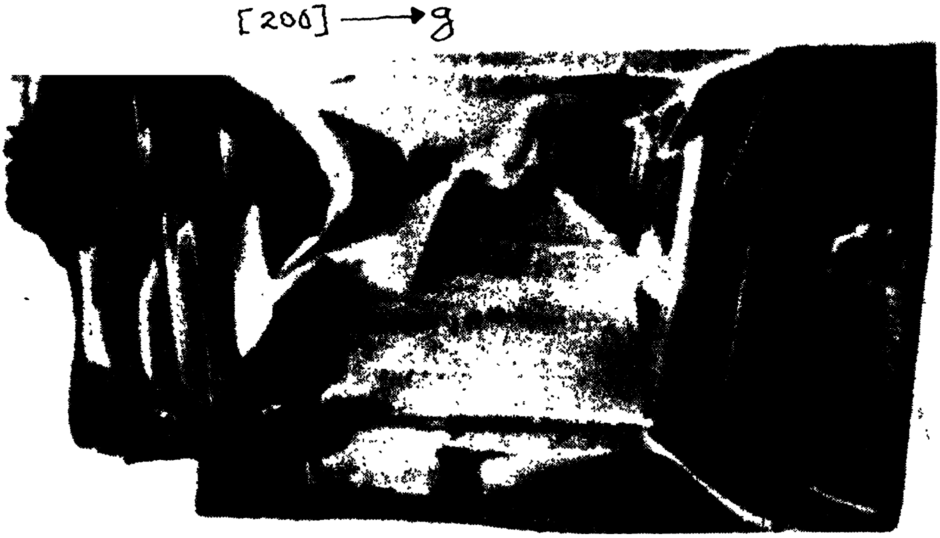
[7] B Matthias and W Mertz *Helv. Phys. Acta.* **19** 222 (1946)

(a)

(b)

Figure 3. X-ray topographs of (001) section of pure ADP crystal for (a) (020) and (b) (022) reflection.

Plate III



(a)

(b)

Figure 4. X-ray topographs of (001) section of mixed KDP-95%–ADP-5% crystal for (a) (200) and (b) (020) reflection.

[8] K B R Varma and K V Ramaiah *Bull. Mater. Sci.* **3** 307 (1981)

[9] M Shanmugham, F D Gnanam and P Ramasamy *J. Mater. Sci. Lett.* **5** 174 (1986)

[10] S Anbukumar, S Vasudevan and P Ramasamy *J. Mater. Sci. Lett.* **5** 224 (1986)

[11] Y Kim, S I Kwun, S Park, B Oh and D Lee *Phys. Rev.* **B28** 3922 (1983)

[12] Y Ono, T Hikita and T Ikeda *J. Phys. Soc. Jpn.* **56** 577 (1987)

[13] S Sen Gupta and S P Sen Gupta *J. Mater. Sci. Lett.* **15** 525 (1996)

[14] I Nitta, R Kiriyama and M Haisa *Sci. Papers (Osaka Univ)* **30** (1951)

[15] S K Mohanlal and R Baskaran *Cryst. Res. Technol.* **22** 21 (1987)

[16] G Ravi, K Srinivasan, S Anbukumar and P Ramasamy *J. Cryst. Growth* **137** 598 (1994)

[17] S Sen Gupta and S P Sen Gupta *J. Mater. Sci. Lett.* **35** 6180 (1996)

[18] A Authier *J. Cryst. Growth* **13/14** 34 (1972)

[19] H Klapper and H Kupers *Acta. Cryst.* **A29** 495 (1973)

[20] A R Lang *J. Appl. Phys.* **29** 597 (1958)

[21] C Belouet, E Dunia and J F Petroff *J. Cryst. Growth* **23** 243 (1974)

[22] C Belouet, M Monnier and J C Verplanke *J. Cryst. Growth* **29** 109 (1975)

[23] C Belouet and W T Stacy *J. Cryst. Growth* **44** 315 (1978)

[24] C Belouet *Prog Cryst. Growth Charact.* **3** 121 (1981)

[25] B Dam and WJP Van Enckevort *J. Cryst. Growth* **51** 607 (1981)

[26] K Srinivasan, P Ramasamy, T Kar and S P Sen Gupta *Mater. Chem. Phys.* **49** 191 (1997)

[27] H L Bhat *Prog. Cryst. Growth Charact.* **11** 57 (1985)

[28] A R Lang *Modern Diffraction and Imaging Technique* eds. S Amelinckx et.al (Amsterdam : North Holland) (1970)

[29] B K Tanner *X-ray Diffraction Topography* (Oxford : Pergamon) (1976)